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Bis(pyrazine-2,3-dicarboxamide)copper(II) Perchlorate

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Abstract. $Cu[C_4N_2H_2(CONH_2)_2]_2(ClO_4)_2$, triclinic, $C\bar{1}$ (a non-standard variant of $P\bar{1}$), $a = 12.21$ (8), $b = 7.65$ (6), $c = 11.06$ (8) Å, $\alpha = 84.75$ (4), $\beta = 101.5$ (5), $\gamma = 96.9$ (5)°, $Z = 2$; $D_x = 1.97$, $D_m = 1.94$ g cm^{-3}; μ(Cu $K\alpha$) = 48·9 cm^{-1}. Anisotropic refinement of 953 photographic data led to $R = 0.09$. The Cu is in a square-planar coordination with one carboxamide O and one pyrazine N from each of a pair of centrosymmetrically related ligands.

Introduction. Previous work on similar complexes, *e.g.* bis(pyridine-2-acetamide)copper(II) perchlorate (Sekizaki, Marumo, Yamasaki & Saito, 1971) and bis(pyrazine-2-carboxamide)copper(II) perchlorate (Sekizaki, 1973), revealed different types of octahedral coordinations for Cu: involving perchlorate O, pyridine N and acetamide O in the former complex, and pyrazine N and carboxamide O in the latter. Thus, with the title compound it was considered worthwhile to find out whether there was an involvement of perchlorate O in the coordination of the Cu and, further, whether the metal atom was coordinated entirely to the carboxamide portions of the ligands, or to both the carboxamide and pyrazine nitrogens. It was also interesting to determine whether the structure was composed of polymeric chains or individual complexes.

Blue prismatic crystals of the compound were kindly supplied by Dr K. Nag of the Department of Inorganic Chemistry of this Institute. Oscillation and zero-layer Weissenberg photographs about the most prominent zone axis of a crystal showed an apparently monoclinic nature. But from higher-layer photographs it could be established that the crystal was a twin, with two triclinic components related by a twofold rotation about the b axis (as the apparently unique axis of the crystal had already been labelled). Almost all the specimens examined were found to suffer from such twinning. Since our original choice of axes accorded a simple description of the nature of twinning, these axes were retained in spite of the fact that they defined a C-centred triclinic cell.

A single specimen was, however, found which was not a twin, and this crystal was used for taking the different oscillation and Weissenberg photographs (both for determining the cell dimensions and for collecting intensity data). Visually estimated intensity data (953 independent reflexions) from eight layers of Weissenberg photographs, taken with filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), about the c axis and the zero layer about the b axis were subjected to the usual corrections (including one for the spot shape) but no absorption correction could be made because of the irregular shape of the specimens.

The measured values of the unit-cell volume (1000 Å^3) and the density of the crystal (1·94 g cm^{-3}) showed that there were two formula units in the C-centred cell. A three-dimensional Patterson synthesis followed by a Fourier map, computed on the basis of the information extracted from the former, revealed the positions of all the non-hydrogen atoms. For refinement by full-matrix least-squares calculations, the neutral-atom form factors of Cromer & Waber (1965) were used and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor $w = 1/\sigma^2(F)$ with $\sigma(F)$, the standard deviation of $|F_o|$, being assumed as follows: for $|F_o| \le 8.0$, $\sigma(F) = 0.15|F_o|$; for $8.0 < |F_o| \le 50.0$, $\sigma(F) = 0.10|F_o|$; for $|F_o| > 50.0$, $\sigma(F) = 0.12|F_o|$. Refinement with isotropic temperature factors reduced R to 0·22; further cycles with anisotropic temperature

Table 1. *Positional parameters* (*as fractions of cell edges*)

E.s.d.'s are listed in parentheses with respect to the least significant digit of any parameter.

	x	y	z
Cu	0	0	0
Cl	0·4448 (2)	0·0913 (4)	0·1786 (4)
O(1)	0·400 (1)	0·206 (1)	0·253 (1)
O(2)	0·541 (1)	0·026 (2)	0·254 (1)
O(3)	0·470 (2)	0·186 (2)	0·070 (2)
O(4)	0·367 (1)	−0·055 (1)	0·147 (1)
O(5)	−0·145 (1)	0·032 (2)	0·015 (1)
O(6)	−0·217 (1)	0·141 (2)	0·377 (1)
N(1)	0·065 (1)	0·167 (1)	0·411 (1)
N(2)	0·032 (1)	0·070 (1)	0·173 (1)
N(3)	−0·257 (1)	0·058 (2)	0·147 (1)
N(4)	−0·087 (1)	0·282 (2)	0·511 (1)
C(1)	−0·054 (1)	0·094 (2)	0·221 (1)
C(2)	−0·037 (1)	0·145 (2)	0·339 (2)
C(3)	0·148 (1)	0·138 (2)	0·358 (2)
C(4)	0·137 (1)	0·091 (2)	0·240 (2)
C(5)	−0·156 (1)	0·062 (2)	0·120 (2)
C(6)	−0·118 (1)	0·194 (2)	0·411 (2)

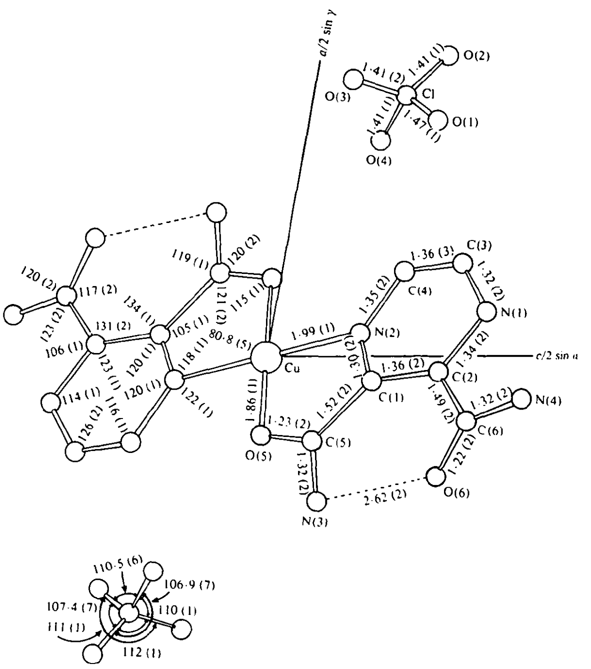

Fig. 1. The title compound projected normal to the *b* axis. Bond lengths (Å) and bond angles (°) with their respective standard deviations are shown.

Table 2. *Equation for the coordination plane and distances of atoms from it with the corresponding standard deviations*

Equation: $0{\cdot}1003X + 0{\cdot}9396Y - 0{\cdot}3271Z = 0.$

N(1)	0·006 (8) Å	C(5)	−0·12 (2) Å
C(3)	0·06 (2)	C(6)	−0·03 (2)
C(4)	0·08 (2)	N(3)	−0·35 (2)
C(1)	−0·08 (1)	N(4)	0·32 (1)
C(2)	−0·06 (2)	O(6)	−0·42 (1)

factors gave the final values of $R = 0{\cdot}09$ with observed reflexions only, and $R = 0{\cdot}10$ including unobserved reflexions.* No attempt was made to locate the H atoms.

Final atomic coordinates are given in Table 1, and interatomic distances and angles are shown in Fig. 1.

Discussion. The structure consists of discrete complexes with Cu in a square-planar coordination involving a ring nitrogen [N(2)] and a carboxamide oxygen [O(5)] from each of a pair of ligands in the *trans* position (Fig. 1). The coordination is strictly planar for reasons of symmetry. The equation of the coordination plane N(2)–O(5)–Cu–O(5′)–N(2′) and the distances of the other atoms in the ligand from this plane are given in Table 2; this shows that the other pyrazine nitrogen [N(1)] also lies on the plane. The pyrazine plane is slightly tilted about the N(1)–N(2) axis, making an angle of 3·5° with the coordination plane. The N(3)–O(6) distance of 2·62 Å indicates a probable hydrogen bond stabilizing the relative orientation of the two carboxamide groups. The perchlorate ion does not coordinate to the Cu atom and, further, it does not even seem to be held to any amide group by hydrogen bonding, as observed in the corresponding pyrazine-2-carboxamide compound (Sekizaki, 1973). The nature of the arrangement in the unit cell is conveniently shown in a projection on to the plane perpendicular to

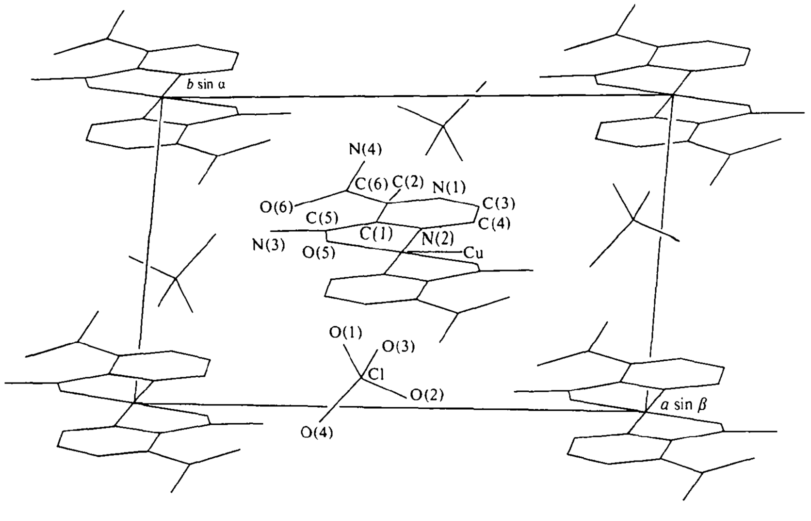

Fig. 2. Arrangement of the molecules projected normal to the *c* axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32549 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the *c* axis (Fig. 2).

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L'Iodure de Zinc–Pyridine (1:2)

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Abstract. $ZnI_2.2C_5H_5N$, monoclinic, $P2_1/c$, $Z = 4$, $a = 9{\cdot}316$ (7), $b = 18{\cdot}034$ (9), $c = 8{\cdot}801$ (7) Å, $\beta = 100{\cdot}8$ (1)°, $V = 1452$ Å^3, $D_c = 2{\cdot}18$, $D_o = 2{\cdot}18$ (2) g cm^{-3}, μ_l(Mo $K\alpha$) = 27·5 cm^{-1}. The zinc atom is tetrahedrally coordinated.

Introduction. Dans le cadre de l'étude thermochimique des composés d'addition des halogénures de zinc, cadmium et mercure avec quelques amines, un certain nombre de résultats ont été obtenus (Le Querler, 1975).

Peu de données structurales ont été publiées sur ces composés. Avec les amines aliphatiques, la mauvaise qualité des cristaux que nous avons obtenus n'a pas permis d'entreprendre des déterminations de structure. Par contre, pour les composés d'addition avec les amines aromatiques, des études de structure ont déjà fait l'objet de publications.

Des cristaux sont obtenus en laissant évaporer à température ambiante la solution obtenue par action de la pyridine sur l'iodure de zinc. Ces cristaux sont en forme d'aiguilles de formule $ZnI_2.2C_5H_5N$, en accord avec l'analyse chimique.

Les diagrammes de Bragg, Weissenberg et Buerger ont permis de déterminer le groupe de symétrie et les valeurs approchées des paramètres cristallins que nous avons précisées à l'aide du diffractomètre.

Les intensités diffractées ont été collectées à l'aide d'un diffractomètre automatique CAD-4 Enraf–Nonius avec le rayonnement $K\alpha$ du molybdène ($\lambda = 0{,}71069$ Å) fourni par un monochromateur à lame de graphite. Les mesures ont été faites jusqu'à l'angle de Bragg $\theta = 30°$. La mesure de trois réflexions de contrôle toutes les heures a montré qu'il n'y avait aucune décomposition du cristal sous les rayons X. Les réflexions ont été corrigées des phénomènes de Lorentz et de polarisation mais nous n'avons pas fait de correction d'absorption ($\mu r = 0{,}5$). Sur 1720 réflexions, seules 1120 satisfaisant au test $I > 4\sigma(I)$ ont été utilisées pour résoudre et affiner la structure.

Par les méthodes directes de Germain, Main & Woolfson (1971), nous avons trouvé les coordonnées des atomes de zinc et d'iode. La méthode de l'atome lourd a permis de localiser les deux atomes d'azote. Dans le reste de la maille cristalline, la densité électronique peu contrastée, n'a pas permis de localiser les autres atomes.

Entretemps, une détermination précise de la structure de $ZnCl_2.2C_5H_5N$ a été publiée (Steffen & Palenik, 1976). Les paramètres des deux composés étant voisins ainsi que les coordonnées des atomes de zinc et d'halogène, nous avons utilisé les coordonnées des atomes du composé $ZnCl_2.2C_5H_5N$ pour affiner la structure de $ZnI_2.2C_5H_5N$.

Après cinq cycles d'affinement avec des facteurs de température isotropes, nous avons obtenu $R = 0{,}077$ et $R_w = 0{,}082$.

Tableau 1. *Coordonnées atomiques* (×10^4)

	x	*y*	*z*
Zn	7793 (2)	1124 (1)	1996 (2)
I(1)	6472 (1)	28 (1)	2951 (1)
I(2)	9963 (1)	1727 (1)	3764 (1)
N(1)	8397 (14)	824 (7)	−37 (15)
C(1)	7621 (18)	293 (10)	−943 (19)
C(2)	7957 (22)	102 (12)	−2404 (22)
C(3)	9099 (19)	430 (8)	−2862 (18)
C(4)	9931 (21)	971 (11)	−1953 (22)
C(5)	9539 (18)	1162 (9)	−517 (19)
N(2)	6269 (11)	1931 (7)	1190 (14)
C(6)	4944 (17)	1758 (9)	547 (27)
C(7)	3866 (20)	2300 (15)	−26 (42)
C(8)	4259 (24)	3008 (12)	46 (31)
C(9)	5618 (23)	3199 (11)	686 (27)
C(10)	6643 (19)	2643 (9)	1257 (23)